APPENDIX F

DISTRIBUTION OF CONTAMINANTS DURING MELTING OF CAST IRON

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DISTRIBUTION OF CONTAMINANTS DURING MELTING OF CAST IRON

This appendix discusses the expected partitioning of contaminants during the production of cast iron. The approach taken here is to use the information developed for partitioning during the melting of carbon steel in electric arc furnaces (EAFs) presented in Appendix E, and by analogy predict the expected behavior of selected trace elements during the production of cast iron. To the extent possible, the deductive process takes into account differences in melting and slagging practice. This discussion should be viewed as a supplement to the information developed in Appendix E. Many of the same references are used as information sources and the detailed thermodynamic discussion is not repeated here.

In order to assess radiation exposures to products made of potentially contaminated cast iron, it is necessary to estimate the partitioning to cast iron of the elements listed in Table 6-3. The present discussion of partitioning during the production of cast iron therefore includes these elements.

F.1 BACKGROUND

Cast iron is an alloy of iron and carbon (ca. 2 to 4.4 wt%) which also typically contains silicon, manganese, sulfur, and phosphorous. The high carbon content of the alloy results in a hard, brittle product which is not amenable to metalworking (as is steel); hence the alloy is cast into the desired end-use form. As noted by the United States Steel Corporation, now USX, (U.S. Steel 1951):

> Castings are of innumerable kinds and uses, roughly grouped as chilled-iron castings, gray-iron castings, alloyed-iron casting, and malleable castings. In general, castings are made by mixing and melting together different grades of pig iron; different grades of pig iron and foundry scrap; different grades of pig iron, foundry scrap, and steel scrap; different grades of pig iron, foundry scrap, steel scrap and ferroalloys, and other metals.

Representative chemical compositions of cast iron are presented in Table F-1.

Cast iron is usually melted in a cupola furnace, an EAF, an electric induction furnace, or an air (reverberatory) furnace. A flow diagram for a typical iron foundry is shown in Figure F-1. The cupola is similar to a small blast furnace where the iron ore in the charge is replaced by pig iron and steel scrap. As described in U.S. Steel 1951:
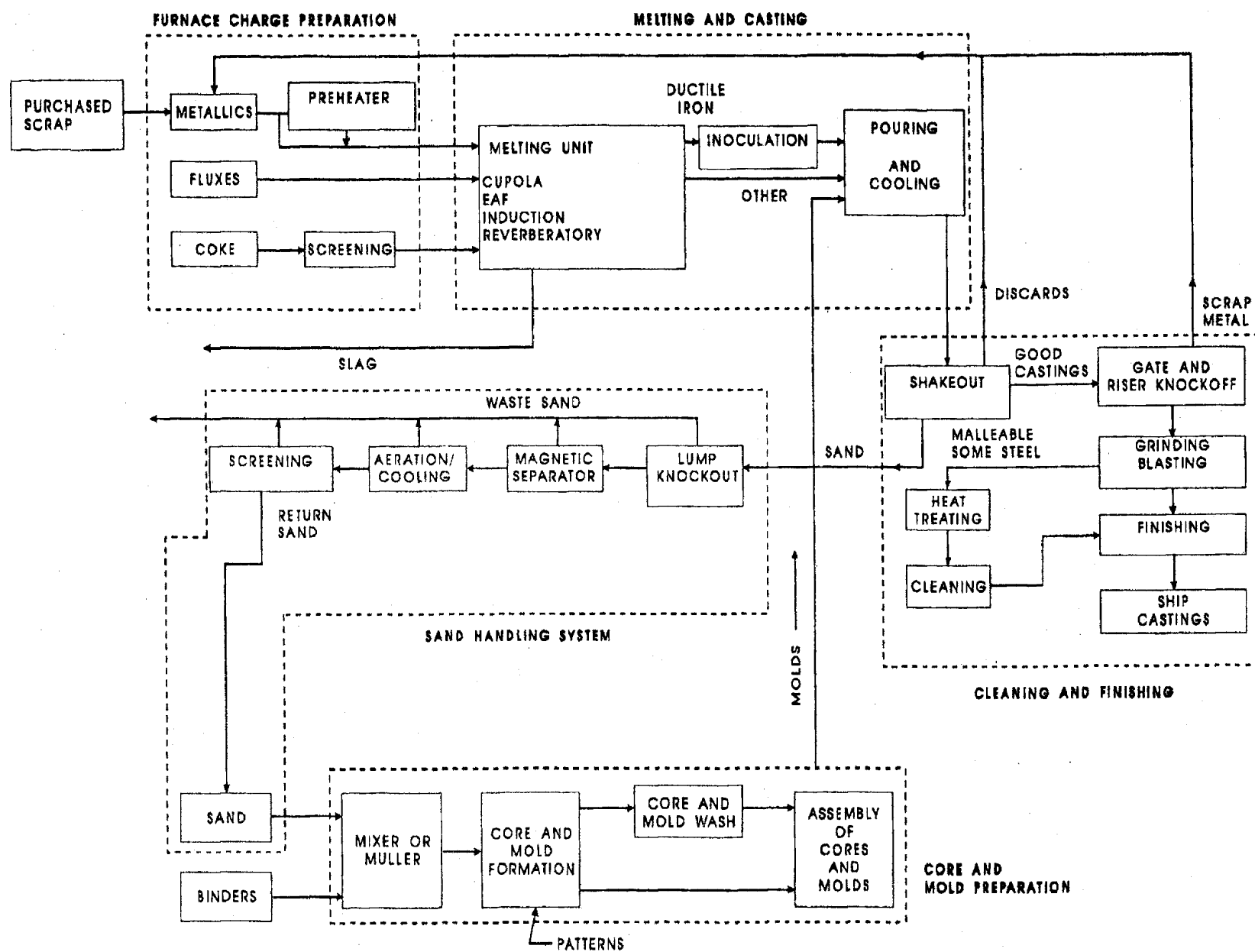
Figure F-1. Flow Diagram of a Typical Cast Iron Foundry (from U.S. EPA 1995)

The charge is composed of coke, steel scrap, and pig iron in alternate layers of metal and coke. Sufficient limestone is added to flux the ash from the coke and form the slag. The ratio of coke to metallics varies depending on the melting point of the metallic charge. Ordinarily, the coke will be about 8 to 10% of the weight of the metallic charge. It is kept as low as possible for the sake of economy and to exclude sulfur and some phosphorus absorption by the metal.

During melting, the coke burns as air is introduced at a 10 to 20 ounce (~0.4 - 0.8 kPa) pressure through the furnace tuyeres. During melting some of the manganese combines with the sulfur forming MnS which goes into the slag. Some manganese and silicon are oxidized by the air blast; the loss is proportional to the amount initially present. Carbon may be increased or reduced depending on the initial amount present in the metallic charge. It may be increased by absorption from the coke or oxidized by the blast. Phosphorus is little affected but sulfur is absorbed from the coke. Prior to casting, the slag is removed from the slag-off hole which is located just below the tuyeres. The molten metal is then tapped through a hole located at the bottom level of the furnace. The depth between these two tapping holes and the inside diameter of the furnace governs the capacity of the cupola (U.S. Steel 1951).

Table F-1. Chemical Composition of Ferrous Castings (wt%)

Element	Gray Iron	Malleable Iron (as white iron)	Ductile Iron	Steel Scrap[a]
C	2.0 - 4.0	1.8 - 3.6	3.0 - 4.0	0.18 - 0.23
Mn	0.40 - 1.0	0.25 - 0.80	0.5 - 0.8	0.60 - 0.90
P	0.05 - 1.0	0.06 - 0.18	< 0.15	≤ 0.40
Si	1.0 - 3.0	0.5 - 1.9	1.4 - 2.0	—
S	0.05 - 0.25	0.06 - 0.20	< 0.12	≤ 0.05

Source: U.S. EPA 1995

[a] Nominal composition of a low carbon steel (e.g., SAE 1020)

The melting temperatures used in producing cast irons are lower than those used in steel making. The melting point of pure iron is 1,538°C (1,711 K), while steel making temperatures are typically about 1,600°C (1,873 K). Furthermore, carbon depresses the melting point of iron: the melting point of an iron alloy containing 3.56% C and 2.40% Si is 1,250°C (1,523 K), while one containing 4.40% C and 0.6% Si has a melting point of 1,088°C (1,361 K) (U.S. Steel 1951).

Fluxing agents added to the furnace charge to promote slag formation include carbonates (e.g., limestone and dolomite), fluorides (e.g., fluorspar), and carbides (e.g., calcium carbide) (U.S.

EPA 1995). Obviously, the furnace environment during the production of cast iron is more highly reducing than that in typical steel melting.

Emissions from the cast iron melting furnaces include particulate matter, CO, SO_2, and small quantities of chlorides and fluorides. These emissions are from incomplete combustion of carbon additives, oxidation of sulfur in coke (for cupola melting), flux additions, and dirt and scale in the scrap charge (U.S. EPA 1995). Melting of ductile iron requires the addition of inoculants such as magnesium in the final stages of melting. The magnesium addition to the molten bath results in a violent reaction and the production of MgO particulates and metallic fumes. Most of these emissions are captured by the emission control system and routed to the baghouse, where the fumes are cooled and filtered. Cupolas are also equipped with an afterburner in the furnace stack to oxidize the carbon monoxide and burn any organics.

In 1998, U.S. shipments of iron and steel castings were (Fenton 1999):

- Ductile iron castings .... 4,070,000 t
- Gray iron castings .... 5,460,000 t
- Malleable iron castings .... 292,000 t
- Steel castings .. .. 1,200,000 t
- Steel investment castings ....83,000 t
- Total .... 11,100,000 t

Scrap consumption by manufacturers of steel castings and by iron foundries and miscellaneous users in that year is summarized below (Fenton 1998):

- Electric arc furnace .... 7,600,000 t
- Cupola furnace .... 7,500,000 t
- Air furnaces and other .... 3,000 t
- Total .... 15,100,000 t

Of this total, 5,800,000 t was home scrap.

In addition, 1,200,000 metric tons (t) of pig iron and 12,000 t of direct-reduced iron were consumed by the iron and steel foundries. The total metal consumption in 1998 was

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16,300,000 t, which is about 47% greater than cast iron and steel shipments. This difference may be due to generation of home scrap. From a recycling perspective, a significant observation is that cast iron contains more than 90% scrap metal.

In 1989, about half of all iron castings were used by automotive and truck manufacturing companies and half of all ductile iron castings were used in pressure pipe and fittings (U.S. EPA 1995).

F.2 MATERIAL BALANCE

Using the results of several studies, EPA (1995) has compiled emission factors for uncontrolled emissions from two types of gray iron foundries:

- Cupola furnace .... 13.8 lb/ton[1] metal
- Electric arc furnace .... 12.0 lb/ton metal

F.2.1 Cupola Furnaces

Based on a 1980 EPA-sponsored environmental assessment of the iron casting industry, Baldwin (1980) reported that a typical cupola producing a medium-strength cast iron from a cold charge would utilize the following materials (as a percentage of iron input):

- Scrap steel 48%
- Foundry returns (i.e., foundry home scrap) 52%
- Ferrosilicon 1.1%
- Ferromanganese 0.2%
- Coke 14%
- Limestone 3%
- Melting loss 2%

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[1] Throughout this appendix, capacities of metal recycling facilities, and other parameters characterizing the metal refining industries will generally be cited in metric tons (tonnes) or, if English units were cited in the source documents, in short tons. The word "ton" will always mean short ton (1 ton = 0.9072 tonne). When practicable, the metric equivalent will also be listed.

Baldwin also documented the quantities of material produced for three foundries: a malleable iron foundry using a induction furnace, a ductile iron foundry using a cupola, and a gray and ductile iron foundry using a cupola for primary melting which duplexes into induction furnaces. The amounts of byproducts are listed in Table F-2.

Table F-2. Amounts of Byproducts from Various Foundries

Byproduct	Amount Generated (lb per ton of metal melted)		
	Malleable Iron	Ductile Iron	Gray and Ductile Iron
Slag	34.5	173	130
Dust Collector Discharge	7.19		78.6

F.2.2 Electric Arc Furnaces

According to a study conducted for EPA, a typical charge for an electric arc furnace (EAF) includes (Jeffery 1986):

- 50% .... 60% scrap iron
- 37% .... 45% scrap steel
- 0.5% .... 1.1% silicon
- 1.3% .... 1.7% carbon raisers[2]

Arc furnaces for cast iron melting range from 500-pound to 65-ton capacity, 25 tons being a common size (Baldwin 1980). According to Jeffery (1986), 94% to 98% of the EAF charge is recovered as iron.

F.2.3 Chemistry Adjustments

As noted in Section F.2.1 and F.2.2, the furnace charge typically contains about 45% steel scrap. If this scrap were similar to that listed in the last column of Table F-1, then, to achieve the cast iron chemistries indicated in that table, it would be necessary to add carbon, phosphorous, sulfur, silicon, and possibly manganese to the furnace charge.

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[2] Carbon raisers are additives introduced into the bath to increase the carbon content of the cast iron, if required.

Production of ductile iron requires making additions to the melt which alter the shape of the graphite particles in the cast iron from flakes to a spheroidal form. Typically, the melt is inoculated with magnesium just before pouring to produce the ductile iron. Much of the magnesium boils off in the process. Sometimes barium, calcium, cerium, neodymium, praseodymium, strontium, and zirconium are also added as inoculants (Baldwin 1980). To reduce the costs of adding magnesium in larger ductile iron production operations, the melt is desulfurized before magnesium is added. This is frequently done by adding CaC_2 (Baldwin 1980).

F.3 PARTITIONING BASED ON REDUCTION OF FeO IN SLAG

As discussed in Section E.4 of Appendix E, an indication of contaminant partitioning between the melt and the slag can be obtained by calculating the free energy change for the reaction

$$\mathbf{M} + \left(\frac{y}{x}\right)\mathbf{FeO} = \left(\frac{y}{x}\right)\mathbf{Fe} + \left(\frac{1}{x}\right)\mathbf{M_xO_y} \qquad \textbf{(F-1)}$$
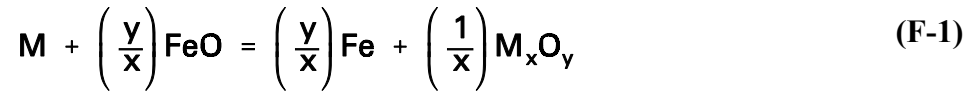
where M is the pure component rather than the solute dissolved in the melt and FeO and M_xO_y are slag components. The standard free energies of reaction of various contaminants with FeO at 1,873 K, a typical temperature for the production of carbon steel in an EAF, were presented in Table E-2. Recalculation of these values for a temperature of 1,573 K, which is typical for cast iron production, indicates no substantive changes from the previous conclusions regarding which elements are expected to concentrate in the slag and which are expected to concentrate in the melt. The assumed 300 K temperature difference between steel melting and cast iron melting produces small changes in the free energies based on Equation F-1, but no significant shifts in the expected equilibria. The free energies of reaction at 1,573 K are listed in Table F-3.

F.4   ADJUSTMENTS TO HENRY'S LAW FOR DILUTE SOLUTIONS

Partition ratios presented in Table E-1 for carbon steel were also recalculated for a furnace temperature of 1,573 K. While slight changes in partitioning ratios were obtained at the lower temperature, no significant shifts in equilibria resulted. An example is the comparable partition ratios for cobalt and uranium, which are shown in Table F-4.

Calculations of partition ratios at 1,573 K are summarized in Table F-5. Values of $\gamma°$ were calculated using temperature-dependent values of the free energy change for transference of the

pure substance to a dilute solution in liquid iron. All values were obtained from Sigworth and Elliot (1974) except cerium, which was taken from JSPS 1988.

Table F-3. Standard Free Energy of Reaction of Various Contaminants with FeO at 1,573 K

Element	Oxide	$\Delta F°$ (kcal)	Comments
$Ac_{(l)}$	Ac_2O_3	-121	Ac should partition to slag
$Am_{(l)}$	Am_2O_3	-105	Am should partition to slag
$Ba_{(l)}$	BaO	-59.6	Ba should partition to slag
$Cs_{(l)}$	Cs_2O		Cs_2O unstable at 1,573 K, Cs should vaporize from melt, some Cs may react with slag components
$Np_{(l)}$	NpO_2	-104	Np should partition to slag
$Pa_{(l)}$	PaO_2	-100	Pa should partition to slag
$Pu_{(l)}$	Pu_2O_3	-89.1	Pu should partition to slag
$Ra_{(g)}$	RaO	-55.0	Ra should partition to slag
$Ru_{(s)}$	RuO_4		Ru should remain in melt
$Sb_{(g)}$	Sb_2O_3		Sb will not react with FeO, some may vaporize from melt
$Sr_{(g)}$	SrO	-65.8	Sr should partition to slag, but low boiling point could cause some vaporization
$Tc_{(s)}$	TcO_2		Tc will not react with FeO, should remain in melt
$Th_{(s)}$	ThO_2	-147	Th should partition to slag
$Y_{(l)}$	Y_2O_3	-104	Y should partition to slag
$Zn_{(g)}$	ZnO		Zn will not react with FeO, Zn should vaporize from melt

Table F-4. Partition Ratios of Two Elements at Typical Iron- and Steel-Making Temperatures

Element	Partition Ratio (N_{MO}/wt% $\underline{M}$)	
	1,573 K	1,873 K
Co	1.0e-4	4.8e-5
U	1.4e+8	8.9e+7

Table F-5. Partition Ratios at 1,573 K for Various Elements Dissolved in Iron and Slag

M	Oxide	γ°_M	$\Delta F^\circ_{f,MO}$ (kcal/mole)[a]	Partition Ratio (N_{MO}/wt%M)
$Ag_{(l)}$	Ag_2O	546	+16.5	1.06e-03[b,c]
$Al_{(l)}$	Al_2O_3	0.013	-280	2.63e+05[b]
$Ca_{(g)}$	CaO	1330	-118	1.15e+10
$Ce_{(l)}$	Ce_2O_3	0.26	-302	1.79e+07[b]
$Co_{(l)}$	CoO	1.08	-25.0	1.00e-04
$Cr_{(s)}$	Cr_2O_3	1.45	-111	1.86e-03[b]
$Cu_{(l)}$	Cu_2O	12.9	-14.0	2.56e-03[b]
$Mn_{(l)}$	MnO	1.36	-64.3	5.24e+00
$Mo_{(s)}$	MoO_3	2.60	-95.3	3.49e-06
$Nb_{(s)}$	Nb_2O_5	1.79	-298	1.22e+05[b]
$Ni_{(l)}$	NiO	0.51	-25.1	4.98e-05
$Pb_{(l)}$	PbO	11900	-17.8	4.56e-02
$Si_{(l)}$	SiO_2	2.7e-4	-143	4.00e+01
$Sn_{(l)}$	SnO_2	3.44	-61.7	3.70e-05
$Ti_{(s)}$	TiO_2	0.035	-159	2.22e+05
$U_{(l)}$	UO_2	0.014	-193	1.44e+08
$V_{(s)}$	V_2O_5	0.078	-228	9.93e+00[b]
$W_{(s)}$	WO_3	1.73	-110	6.56e-05
$Zr_{(s)}$	ZrO_2	0.029	-191	4.52e+08

[a] $\Delta F^\circ_{f,FeO}$ = -38.1 kcal/mole

[b] PR $= N^{1/2}$/wt% M

[c] Ag will not react with FeO, Ag_2O unstable at 1,573K

F.5   OBSERVED PARTITIONING DURING METAL MELTING

F.5.1   General Observations

Because of concerns that tramp elements might be accumulating in cast irons from contaminants in steel scrap and affecting casting behavior, the U.S. Bureau of Mines conducted an extensive study over a period of more than five years to evaluate the impurities in cast iron (Natziger et al. 1990). While this study does not specifically address partitioning, the results can provide confirmation of inferred partitioning. Samples were obtained from 28 ductile iron foundries and

52 gray iron foundries at various times over the course of the study. The distribution of foundries by geographical location, furnace type and product is shown in Table F-6.

Table F-6. Distribution of Foundries in Bureau of Mines Tramp Element Study

Zone	Ductile Iron						Gray Iron					
	Furnace Type			Size[a]			Furnace Type			Size[a]		
	Cupola	Electric	Induction	A	B	C	Cupola	Electric	Induction	A	B	C
Northeast	1	0	2	1	1	1	6	0	2	3	5	0
Great Lakes	5	0	2	1	2	4	12	0	2	4	7	3
Southeast	1	1	3	3	1	1	4	0	3	3	2	2
Upper Midwest	4	1	3	0	8	0	11	1	4	0	12	4
West	1	0	4	5	0	0	3	1	3	5	1	1

Source: Natziger et al. 1990
[a] A: < 1,000 tons per month; B: 1,000 to 8,000 tons per month; C: >8,000 tons per month

With limited exceptions, cerium, niobium, lead, and antimony were not found at the limits of detection (wt%) listed below for the 23 calendar quarters over which sampling was conducted:

- Ce .... 0.02 - 0.1
- Nb .... 0.01 - 0.05
- Pb .... 0.005 - 0.2
- Sb .... 0.02 - 0.1

Lead levels above the lower detection limit were observed in four quarters, as shown in Table F-7.

Table F-7. Lead Levels at Two Different Types of Foundries

Quarter	Pb Above Detection Limits (wt%)	
	Ductile Iron	Gray Iron
1	0.005−0.007	< 0.005−0.007
2	< 0.005−0.008	< 0.005−0.010
3		< 0.005−0.006
20		< 0.005−0.007

Source: Natziger et al. 1990

Average analyses for other elements of interest are included in Table F-8.

Table F-8. Average Concentrations of Tramp Elements in Cast Iron (wt%)

Zone	Ductile Iron					Gray Iron				
	Co	Mn	Mo	Ni	Zn	Co	Mn	Mo	Ni	Zn
Northeast	0.008	0.378	0.020	0.067	0.003	0.009	0.726	0.025	0.073	0.002
Great Lakes	0.007	0.405	0.022	0.117	0.003	0.010	0.703	0.051	0.192	0.002
Southeast	0.009	0.453	0.017	0.171	0.004	0.010	0.675	0.030	0.142	0.003
Upper Midwest	0.008	0.409	0.024	0.257	0.002	0.009	0.701	0.040	0.107	0.002
West	0.012	0.415	0.025	0.186	0.005	0.009	0.670	0.040	0.086	0.002

Source: Natziger et al. 1990

F.5.2   Antimony

Thermodynamic calculations based on Equation F-1 indicate that antimony will not partition to the slag. Experimental work by Kalcioglu and Lynch (1991) showed that when antimony is added to carbon-saturated iron at 1,723 K and allowed to react with an acidic slag (basicity ratio = 0.666), the resulting partition ratios were those listed in Table F-9.

Table F-9. Distribution of Antimony Between Slag and Metal

[wt%Sb][a]	L_{Sb}[b]
0.45	0.067
0.87	0.022
1.03	0.020
1.06	0.018

[a] [wt%Sb] = concentration in metal

[b] L_{Sb} = (wt%Sb)/[wt%Sb]
(wt%Sb) = concentration in slag

Based on these values for L_{Sb} and an assumed slag-to-metal mass ratio of 0.05, the quantities of antimony in the slag are insignificant (i.e., <1%). Antimony recoveries ranged from 47% to 71% for these four tests, the losses being presumably due to vaporization.

Nassaralla and Turkdogan (1993) cite the following equation for the activity of antimony in carbon-saturated iron:

$$\log \gamma_{Sb}^o = -\frac{6623}{T} + 5$$

This yields a value for γ° of 6.2 at 1,573 K, which, when combined into the Henry's Law relationship, indicates that the partition ratio, $\dfrac{(N_{Sb_2O_3})^{1/2}}{[wt\% \ Sb]}$, is 2.6 x 10^{-5}, supporting the view that antimony partitions strongly to the melt. Although, as noted in Section F.5.1, no antimony was found in cast iron samples at the lower limit of detection (0.02 - 0.1 wt%), this does not necessarily vitiate the thermodynamic partitioning argument. Antimony may not be present in the feed materials at the detection limit. Although some antimony may vaporize from the melt, insufficient evidence is available to quantify this possibility. To avoid possibly underestimating exposures to cast iron products potentially contaminated with antimony, antimony is assumed to remain in the melt.

F.5.3   Carbon

As was noted in Sections F.2.1 - F.2.3, carbon is added to the furnace charge to achieve the levels desired in the finished product (e.g. 1.8% to 4.0% C). During the melting process, some of the carbon in the scrap steel may be oxidized and removed from the system as CO; however, there is a net addition of carbon to the melt, rather than a net removal. Since it is impossible to predict how much carbon is removed from the scrap steel and later replaced with carbon from other charge materials, it is conservatively assumed that all the carbon in the scrap remains in the cast iron.

F.5.4   Cerium

Cerium is sometimes used as an inoculant in ductile irons (Baldwin 1980); consequently, small amounts must remain in the melt, in spite of the fact that thermodynamic calculations suggest that cerium partitions strongly to the slag. In addition, as noted in Section F.5.1, cerium was not found in cast iron at the limits of detection in samples from 28 ductile iron foundries. Given this conflicting information, the most likely situation is that minute amounts of cerium will remain in the cast iron. However, no evidence has been uncovered which suggest that the amount of cerium remaining in the melt is greater than 0.5% of the total.[3]

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[3] Partition ratios in the present analysis are calculated to the nearest 1%. Thus, any partition ratio less than 0.5% is assigned a value of zero.

F.5.5   Cesium

Cesium is expected to partition to the slag and to accumulate in the baghouse dust. None is expected to remain in the melt (Harvey 1990).

F.5.6   Iron

Some iron is expected to be oxidized and to transfer to the slag. However, no detailed composition data have been located in this study to permit quantification of this expected partitioning. Therefore, it is conservatively assumed that no iron partitions to the slag.

F.5.7   Lead

Based on thermodynamic equilibrium calculations, lead is expected to remain in the melt. However, lead has very limited solubility in liquid iron. Furthermore, it has a vapor pressure of 0.01 atm at 1,408 K (Darken and Gurry 1953) and 0.05 atm at 1,462 K (Perry and Green 1984). At the limits of detection, lead is seldom found in cast iron (see Section F.5.1).

Lead has been detected in leachates from baghouse dust collected by cupola emission control systems. Leachate levels based on the EP toxicity test ranged from about 10 to about 220 mg/L (Kunes et al. 1990). Since it is not possible to quantitatively relate these leachate results to contaminant levels in the dust, one can only reach the qualitative conclusion that some lead vaporizes from the cast iron melt and is collected in the baghouse.

The combined evidence indicates that, for the purposes of the present analysis, lead can be assumed to completely vaporize from the melt.

F.5.8   Manganese

Based on thermodynamic calculations which assume that $\gamma^{\circ}_{Mn} = 2.6$, the partition ratio of manganese between slag and iron is calculated to be about 5 at 1,573 K (see Table F-5), which suggests that significant amounts of manganese will be present in both the slag and the melt. Meraikib (1993) determined that during steelmaking, the distribution of manganese between the slag and the melt could be described by the equation

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$$\eta_{Mn} = \frac{(Mn)}{[Mn]}$$

$$= a_{[O]} f_{[Mn]} \exp\left(\frac{27530}{T} - 0.0629\,B - 7.3952 \right)$$

(Mn) = concentration of manganese in slag (wt%)

[Mn] = concentration of manganese in melt (wt%)

$a_{[O]}$ = activity of oxygen in melt

$f_{[Mn]}$ = activity coefficient for [Mn]

T = absolute temperature (K)

B = slag basicity

Although there are risks in extrapolating this equation to cast iron melting, the calculation was undertaken in the absence of better information. Partition ratios at two different partial pressures of CO were estimated, assuming T = 1,573 K, B = 0.63, $f_{[Mn]}$ = 0.95, and 130 lb of slag generated per ton of metal melted. These values are listed in Table F-10.

Table F-10. Partition Ratios of Manganese at Different Partial Pressures of CO

P_{CO} (atm)	η_{Mn}	Partition Ratio (see text) (mass in slag/mass in metal)
1	0.45	0.03
0.1	0.045	0.003

Note: The oxygen activity is calculated using free energy values for C and O dissolved in iron (JSPS 1988) and the CO free energy of formation given by Glassner (1957). The calculated values are in close agreement with information presented by Engh (1993, p. 67).

F.5.9   Niobium

On the basis of thermodynamic calculations, niobium is expected to partition primarily to the slag. However, according to Harvey (1990), niobium can be retained in steel under reducing conditions. The expected reaction is

$$2\underline{Nb} + 6\underline{O} + Fe = FeO \cdot Nb_2O_5$$

F-14
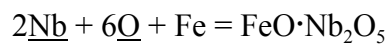
where the elements on the left side of the equation are melt constituents and the compound on the right is a slag constituent. The equilibrium constant for the reaction is

$$K_1 = \frac{a_{FeO \cdot Nb_2O_5}}{a_{Fe} \, a_{Nb}^2 \, a_O^6} = 2.4 \cdot 10^{10} \qquad (T = 1,873K)$$

Assuming that $\dfrac{a_{FeO \cdot Nb_2O_5}}{a_{Fe}} = 1$, values of a_{Nb} corresponding to two assumed values of a_O were calculated, as listed below:

a_O	a_{Nb}
1	6.5e-6
0.01	6.5

The value of K_{1573}, the equilibrium constant at 1,573 K, is not available; however, based on the values of the free energies of formation of Nb_2O_5 at 1,573 K and 1,873 K, it is expected that $K_{1573} > K_{1873}$. Thus, a highly reducing environment ($a_O \ll 1$) would be required to retain niobium in the melt at the lower temperature.

As noted in Section F.5.1, niobium is not detected in cast iron at the detection limit, which indicates that either there are no significant quantities of niobium in steel scrap or the typical melting conditions are not sufficiently reducing to cause niobium to be retained in the melt.

F.5.10 Zinc

Under steelmaking conditions, zinc is expected, from a free energy perspective, not to partition to the slag and, because of its high vapor pressure, to vaporize from the melt to a large extent. Cast iron melting temperatures, though lower, are still well above the normal boiling point of zinc (1,180 K).

Based on information presented by Perrot et al. (1992), the solubility of zinc at 1,573 K is expected to be about 140 ppm when the partial pressure of zinc is 10^{-2} atm. Silicon in the cast iron will tend to increase the zinc solubility while manganese will have the opposite effect. As noted in Section F.5.1, from 20 to 50 ppm of zinc are typically found in cast iron, which suggests that it is unrealistic to assume that 100% of the zinc volatilizes and collects in the baghouse.

Assume, for example, that a furnace charge contains 45% steel scrap and 55% cast iron scrap, and that both the cast iron scrap and the product contains 30 ppm Zn, as listed in Table F-8. If the steel scrap contains less than 0.67 wt% Zn, then 1% or more of the zinc would remain in the melt (see Note 3) (Koros 1994).

According to Koros (1994), typical galvanized scrap contains about 2% Zn. The same author reported that, in 1992, 35% of the scrap classified as No. 1 bundles and busheling is galvanized steel. Other grades of scrap likely to contain significant quantities of galvanized steel include shredded scrap and No. 2 bundles (Fenton 1996). For 1993, No. 1 bundles, No. 1 busheling, shredded, and No. 2 bundles accounted for 46% of the carbon steel scrap used in iron foundries (Bureau of Mines 1995). Using the above information, it can be estimated that about 2% of the zinc will remain in the cast iron and the balance will be transferred to the baghouse dust, based on the following calculation:

$$P_{Fe}^{Zn} = \frac{C_{Fe}^{Zn}}{f_{Fe}^{Fe'} C_{Fe'}^{Zn} + f_{Fe}^{s} f_{s}^{g'} f_{g'}^{g} C_{g}^{Zn}}$$

P_{Fe}^{Zn} = partition fraction of zinc in cast iron
= 0.0205

C_{Fe}^{Zn} = mass fraction of zinc in cast iron product
= 3×10^{-5}

$f_{Fe}^{Fe'}$ = mass ratio of cast iron scrap : cast iron product
= 0.55

$C_{Fe'}^{Zn}$ = mass fraction of zinc in cast iron scrap
= 3×10^{-5}

f_{Fe}^{s} = mass ratio of steel scrap : cast iron product
= 0.45

$f_{s}^{g'}$ = fraction of galvanized-steel-bearing scrap sources in steel scrap
= 0.46

$f_{s}^{g'}$ = fraction of galvanized steel in galvanized-steel-bearing scrap sources
= 0.35

C_{g}^{Zn} = mass fraction of zinc in galvanized steel
= 0.02

F.6   PARTITIONING SUMMARY

F.6.1   Elements Which Partition to the Melt

It is assumed that 1% of the total melt will be transported from the furnace and collected in the baghouse. This is approximately the geometric mean of the values for two types of foundries listed in Table F-2 and is consistent with the values cited in U.S. EPA 1995 (see Section F.2). Based on thermodynamic equilibria, the following elements are expected to partition 99% to the melt and 1% to the baghouse dust: cobalt, molybdenum, nickel, ruthenium, and technetium.

Free energy calculations also suggest that silver partitions to the melt but, for EAF melting of carbon steel, this information was tempered by the facts that silver has a significant vapor pressure at steelmaking temperatures (10^{-2} atm at 1,816 K) and some work on stainless steel melting done at Studsvik (Menon et al. 1990) had shown silver in the baghouse dust. However, the vapor pressure of silver is at least an order of magnitude lower at temperatures used in cast iron melting (e.g., 10^{-3} atm at 1,607 K)(Darken and Gurry 1953). Consequently, in cast iron, silver is assumed to partition 99% to the melt and 1% to the baghouse dust.

Although there is reason to suspect that some niobium might be found in the melt under highly reducing conditions, no evidence was uncovered to support that supposition.

For reasons discussed in Section F.3.3 above, carbon and antimony are expected to remain in the melt except for small quantities contained in dust transferred to the baghouse (i.e., 1%).

Manganese is predicted to remain primarily in the melt. It is expected that no more than about 2% of the manganese will partition to the slag.

Most of the zinc is expected to volatilize and be collected in the baghouse. Only about 2% is assumed to remain in the melt.

Table F-11 lists the partition ratios of elements which are expected to show significant (i.e., at least 1%) partitioning to the melt.

F.6.2 Elements Which Partition to Slag

For those elements which are strong oxide formers and are expected to partition to the slag, the assumption is made here that 5% of the slag will be transported to the baghouse as dust. This is the same assumption as made for melting carbon steel in electric arc furnaces. Based on this assumption, thermodynamic equilibrium calculations at 1,573 K and chemical analogies, the following elements are expected to partition 95% to the slag and 5% to the baghouse dust: Ac, Am, Ce, Cm[4], Eu[4], Nb, Np, Pa, Pm[4], Pu, Ra, Sr, Th, and U.

Table F-11. Proposed Partitioning of Metals Which Remain in the Melt

Element	Distribution (%)		
	Melt	Slag	Baghouse
Ag	99		1
C	99		1
Co	99		1
Fe	99		1
Mn	97	2	1
Mo	99		1
Ni	99		1
Ru	99		1
Sb	99		1
Tc	99		1
Zn	2		98

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[4] Since thermodynamic data were not available for these elements, partitioning was assumed to be analogous to similar elements in the rare-earth and actinide series in the periodic table.

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